EFFECT OF THE DEGREE OF DVB CROSSLINKING ON THE METAL ION SPECIFICITY OF POLYACRYLAMIDE-SUPPORTED GLYCINES

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ABSTRACT

Metal ion specificity studies of divinylbenzene (DVB)-crosslinked polyacrylamide-supported glycines in different structural environments were investigated. The effect of the degree of crosslinking on the specific rebinding of the desorbed metal ion was investigated towards Co(II), Ni(II), Cu(II), and Zn(II) ions. The metal ion-desorbed resins showed specificity for the desorbed metal ion and the specificity characteristics increases with an increasing degree of the crosslinking agent. The polymeric ligands and metal complexes were characterized by IR, UV-visible and EPR spectra, and by SEM analysis. The swelling and solvation characteristics of the crosslinked polymers, polymeric ligands and metal complexes, the effect of the pH dependence on metal ion binding and rebinding and the kinetics of metal ion binding and rebinding were also followed. The complexation resulted in the downfield shift of the carboxylate peak in the IR spectra. The EPR parameters are in agreement with a distorted tetragonal geometry. The Cu(II) ion-desorbed resins selectively rebinds Cu(II) ions from a mixture of Cu(II) and Co(II) and Cu(II) and Ni(II) ions. The resin could be regenerated several times without loss of capacity and effective for the specific and selective rebinding of Cu(II) ions.

Key Words: Polymer-supported; Degree of crosslinking; Metal ion complexation; Metal ion specificity; Selectivity.

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INTRODUCTION

Chelating resins, with selective complexation properties have extensive attraction, since they can achieve effective separation of metal ions [1-4]. It is possible to design chelating polymers with optimum physicochemical properties for the separation of metal ions by the suitable selection of monomers and crosslinking agents. The nature of monomers and the relative rigidity and flexibility of the crosslinking agent has a significant effect on the complexing ability of the developed metal ion specific polymers. A proper understanding of the interdependence of functional group reactivity and molecular architecture of the polymer support is of great interest in the designing of tailor-made polymers for specific applications. Information regarding the precise microenvironment of the ligand could be possible in well-defined systems. This, in turn, would help in the design of selective complexation of metal ions by polymeric ligands. However, the conventional chelating resins have problems including low binding selectivities, slow rebinding kinetics and loss of selectivity with time [5-7]. The metal ion specific polymers proposed recently is having high selectivity and specificity than the conventional chelating resins.

Recently, we have reported the remarkable metal ion specificity studies of metal ion-desorbed crosslinked polyacrylamide-supported glycines with N, N'-methylene-bis-acrylamide (NNMBA) crosslinking [8]. Since the specificity of the metal-ion desorbed system depends on the rigidity of the polymer-support, in the present study, we have selected a more rigid and hydrophobic divinylbenzene (DVB) crosslinking agent. As expected, polyacrylamide-supported glycines with DVB crosslinking has been found to be more effective than the NNMBA-crosslinked system. The study describes the detailed investigations of the preparation of crosslinked polymers, incorporation of ligand functions, optimization of the conditions of metal ion complexations, characterization by various physicochemical methods and the effect of the memory of the metal ion-desorbed systems for the specific and selective separation of metal ions. The results of these studies are correlated with the degree of DVB crosslinking in the polymer support.

EXPERIMENTAL

Materials and Methods

Divinylbenzene (DVB) was purchased from Aldrich Chemical Company, USA. The metal salts used were cobalt chloride, nickel sulfate, copper sulfate and zinc sulfate. All the other low molecular weight compounds were commercially available, and were purified by the literature procedure unless otherwise specified. The FT-IR spectra were recorded on a Bruker IFS-55 spectrophotometer using

KBr pellets. UV-vis. spectra were recorded on a Shimadzu UV-160A spectrophotometer. EPR spectra were recorded at 303 K with a Varian E-12 spectrometer. SEM photographs were taken on a Hitachi S-2400 instrument.

Preparation of 2-20 Mol% DVB-Crosslinked Polyacrylamides

Divinylbenzene was washed with a 1% NaOH solution and water to remove the inhibitor. Acrylamide and divinylbenzene were dissolved in ethanol (80 mL), benzoyl peroxide (500 mg) was added to the solution and it was heated on a water bath with stirring. Heating and stirring were continued until the polymer precipitated. The resin was collected by filtration, washed several times with water, ethanol, benzene, and methanol. The resin was dried in an oven at 70°C. Polymers with 2, 4, 8, 12, and 20 mol% of DVB crosslinks were prepared by varying the composition of monomers.

Transamidation of Polyacrylamides with Sodium Salt of Glycine

Crosslinked polyacrylamide (10 g) was treated with excess sodium salt of glycine [glycine (20 g) and NaOH (10.64 g) in water (50 mL)] at 100°C for 20 hours. The reaction mixture was poured into water containing crushed ice. The functionalized polymers were collected by filtration in a soxhlet using methanol and acetone, and dried in an oven at 50°C.

Estimation of Carboxyl Capacity

The carboxylate polymers (100 mg) were equilibrated with HCl (0.2N, 10 mL) with stirring for 24 hours. The resin samples were filtered, washed with distilled water to remove unreacted HCl, and the filtrate was titrated against NaOH (0.2 N) to a phenolphthalein end point.

Metal Ion Complexation of Polyacrylamide-Supported Sodium Salt of Glycine: General Procedure

The crosslinked carboxylate polymers (100 mg) were stirred with a metal salt solution (0.05 N, 50 mL) for 24 hours. The complexed resins were collected by filtration and washed with excess distilled water to remove uncomplexed metal ions. The concentration of Co(II), Ni(II) and Cu(II) solutions were followed by UV-visible spectrometry and Zn(II) by a complexometric method.

Desorption of Complexed Metal Ions: General Procedure

The complexed metal ions were desorbed using H_2SO_4 (0.2 N), and the acid treated resins were washed with distilled water to remove unreacted HCl and neutralized using dilute NaOH (0.2 N).

Effect of pH Dependence on Metal Ion Binding and Rebinding

To different sets of crosslinked carboxylate polymer samples (100 mg) metal salt solutions at different pH were added and stirred. The metal ion binding studies were carried out by placing in a thermostated shaker for 24 hours. The uncomplexed metal ions were washed using distilled water and analyzed as described earlier. The same experiment was repeated for metal ion-desorbed systems.

Swelling Studies of 2-20 Mol% DVB-Crosslinked Polyacrylamides, Polyacrylamide-Supported Glycines and Cu(II) Complexes: General Procedure

The crosslinked polyacrylamides 200 (mg) were equilibrated with 50 mL distilled water for 48 hours. The swollen resins were collected by filtration, adhering traces of water were removed carefully by wiping with a blotting paper, and the swollen weight was determined. The samples were then dried in vacuum. The equilibrium water content (EWC) was calculated as the ratio of the water in the gel to the total weight of the hydrated gel expressed as percentage by the following equation:

$$EWC = \frac{\text{Weight of wet resin} - \text{Weight of dry resin}}{\text{Weight of wet resin}} \times 100$$

Kinetics of Metal Ion Binding and Rebinding: General Procedure

To different sets of crosslinked resins (100 mg) copper sulfate solution (0.05 N, 50 mL) was added and shaken in a thermostat for different time intervals at 30°C and 40°C. The metal ion binding experiments were followed by UV-visible spectrometry. The same experiment was repeated for metal ion rebinding also.

Rebinding of Metal Ions: General Procedure

The neutralized metal ion-desorbed resins were treated with metal salt solutions of the desorbed metal ion (0.05 N, 50 mL), and other metal ions and the extent of complexations were followed as described earlier.

Selectivity Studies: General Procedure

To each of the metal ion-desorbed polyacrylamide-supported glycine ligands, a mixture of metal ions: $CuSO_4.5H_2O$ (50 mL) + $CoCl_2.6H_2O$ (50 mL); and $CuSO_4.5H_2O$ (50 mL) + $NiSO_4.6H_2O$ (50 mL) was added and stirred for 24 hours. The amount of different metal ions complexed were estimated by multi-component UV-visible spectrometry.

RESULTS AND DISCUSSION

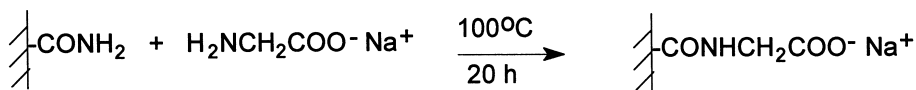### Preparation of 2-20 Mol% DVB-Crosslinked Polyacrylamides

Polyacrylamides with 2-20 mol% DVB crosslinks were prepared at 70°C by free radical solution polymerization of the monomers in ethanol using benzoyl peroxide as the initiator as represented in Scheme 1. The commercial sample of DVB which contains 65% *p*-divinylbenzene, was used for polymerization. DVB was washed with 1% NaOH solution to remove the inhibitor, washed with water and finally dried over anhydrous sodium sulfate. With an increasing degree of crosslinking, the swelling characteristics in water decreases, and the resin becomes more powdery in nature. Compared to the hydrophilic crosslinked system, the DVB-crosslinked system shows higher swelling in organic solvents. This would favor the reactions which are to be carried out in organic media [9].

Preparation of 2-20 Mol% DVB-Crosslinked Polyacrylamide-Supported Glycines

Crosslinked polyacrylamides with a varying degree of crosslinking were converted to polyacrylamide-supported sodium salt of glycines by transamidation with excess sodium salt of glycine at 100°C for 20 hours (Scheme 2). The sodium salt of glycine was prepared by mixing a equimolar amount of glycine and sodium hydroxide. The resin was washed with distilled water, methanol, and acetone. Washings were continued till the resin was free from glycine and sodium hydroxide confirmed by ninhydrin test of the washings and by litmus test.
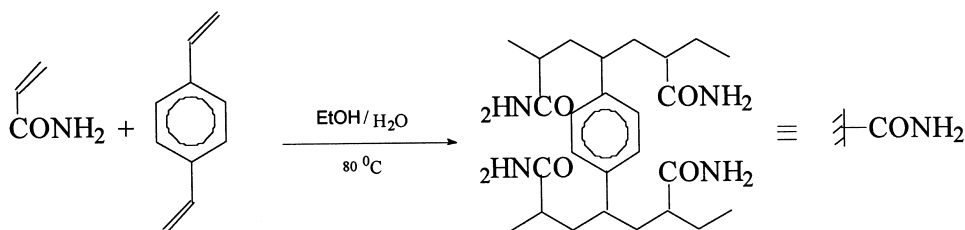
Scheme 1. Preparation of DVB-crosslinked polyacrylamides.

$$\text{-CONH}_2 \ + \ \text{H}_2\text{NCH}_2\text{COO}^-\text{Na}^+ \ \xrightarrow[\text{20 h}]{100^\text{O}\text{C}} \ \text{-CONHCH}_2\text{COO}^-\text{Na}^+$$

Scheme 2. Preparation of polyacrylamide-supported sodium salt of glycines.

In the case of a DVB-crosslinked system, the decrease in carboxyl capacity with increasing crosslinking is notably sharp, as represented in Figure 1. The ligand capacity is higher for low crosslinked systems and decreases with increasing degree of crosslinking. As the degree of crosslinking increases, the availability of the amide groups buried within the crosslinks decreases leading to a decrease in the carboxyl capacity. Moreover, the rigid and hydrophobic nature of DVB crosslinks hinders the permeation of polar glycine molecules to the interior of crosslinked polyacrylamide matrix.

Metal Ion Complexations of 2-20 Mol% DVB-Crosslinked Polyacrylamide-Supported Sodium Salt of Glycines

The complexation of a polymer-supported ligand is influenced by the characteristics of the macromolecular matrix like the nature and extent of crosslinking agent, nature of the polymer backbone and separation of the ligand functions from the polymer-matrix [10, 11]. In order to investigate the effect of the degree of DVB crosslinking on the metal ion complexation of carboxylate functions supported on 2-20 mol% DVB-crosslinked polyacrylamides, complexations of Co(II), Ni(II),
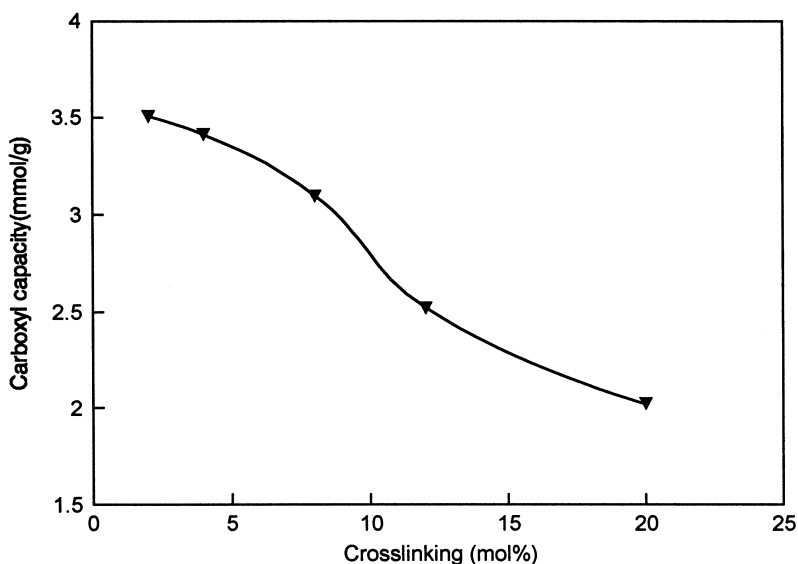

Figure 1. Carboxyl capacity vs. extent of DVB crosslinking.

Cu(II), and Zn(II) ions were carried out by a batch equilibration method. For all complexation studies, a definite weight of the polymeric ligand was equilibrated with an excess metal salt solution of a known concentration. The concentration of Co(II), Ni(II), Cu(II) and Zn(II) ions were followed as described earlier.

The extent of DVB crosslinking has a significant effect on the interaction of its ligands with metal ions. As the degree of rigid and hydrophobic DVB crosslinks increases, the metal ion intake decreases as shown in Figure 2. The observed trend in metal ion complexation is: Cu(II) > Ni(II) > Co(II) > Zn(II). From the results, it is clear that the degree of DVB crosslinking exerts a striking influence on the metal ion complexation of carboxylate ligands supported on DVB-crosslinked polyacrylamides. The availability of the ligands for the metal ions decreases with increasing DVB content. A similar decrease in the reactivities of DVB-crosslinked polyacrylamide-supported ligands and reagents are reported [12, 13].

Characterization of Unfunctionalized and Functionalized Polyacrylamides, and Their Metal Complexes

FT-IR Spectra

The FT-IR spectra of the crosslinked polyacrylamides showed the amide -N-H and C=O at 3500 and 1653 cm^{-1}, respectively. The peak at 800 cm^{-1} corresponds to the aromatic ring in the DVB crosslinking agent. In the functionalized polymer, the carboxylate group absorbs strongly at 1667 cm^{-1} and weakly at 1400 cm^{-1}. These bands originate from the asymmetric $(C....O)_2$ stretching of the carboxylate
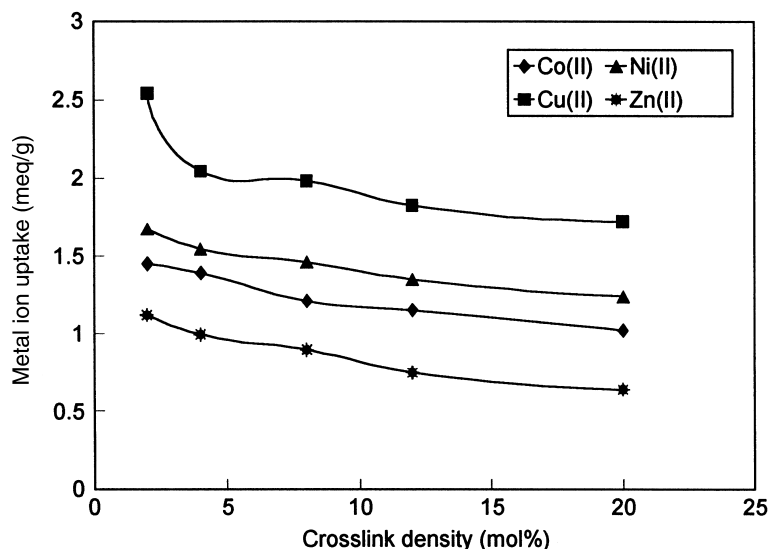

Figure 2. Metal ion complexation of 2-20 mol% DVB-crosslinked polyacrylamide- supported glycines.

group. Complexation with metal ion is reflected in the shift of absorption peak at 1667 cm^{-1} to 1643 cm^{-1}. Metal ion coordination of carboxylate groups and weakens its double bond character [14]. Similar observations of shifts in the carboxyl group frequencies on complexation are reported [15, 16].

UV-Visible Spectra

The structure and geometry of a polymer metal complex is largely determined by the microenvironment of the polymer domain [17]. The polymer anchored Co(II) complex exhibits bands at 9611-9685 cm^{-1} and 18315-19417 cm^{-1} due to $^4T_{1g}$ (F)-$^4T_{2g}$ (F) (γ_1) and $^4T_{1g}$ (F) - $^4T_{1g}$ (P) (γ_3) transitions in an octahedral geometry. In polymer anchored Ni(II) complexes, there are three spin allowed transitions $^3A_{2g}$ -$^3T_{2g}$ (P), 13531-15174 cm^{-1} and $^3A_{2g}$ -$^3T_{1g}$ (F), 24752-25380 cm^{-1} and $^3A_{2g}$ -$^3T_{1g}$ (P), 33222-45045 cm^{-1} give near octahedral geometry. Due to Jahn-Teller distortions, the d^9 configuration of the Cu(II) ion complexed polymer, a distorted octahedral structure is obtained. xy-x^2-y^2 and xz, yz-x^2-y^2 transitions occur as the axial bond is lengthening and xy-x^2-y^2 transition shifts to blue region. Tetragonal Cu(II) complex is expected to show the transition $^2B_{1g}$ - $^2A_{1g}$, $^2B_{1g}$ - $^2B_{2g}$, and $^2B_{1g}$ - $^2E_{2g}$ but, bands due to these transitions overlap to give one broad band [17]. The broad band observed in the region 19626-21800 cm^{-1} indicates the tetragonal type symmetry for Cu(II) complex. In polymer anchored Zn(II) complex, the spectra obtained is ligand related and no d-d transitions occurs. Therefore, it would have a tetrahedral geometry.

EPR Spectra

The EPR spectral pattern of paramagnetic Cu(II) complexes is influenced by the number of coordinating ligands as well as the geometry of the complex [18, 19]. The magnetic parameters are assigned using 2,2-diphenyl-1-picryl hydrazyl (DPPH) as the reference. The g values of Cu(II) complex of polymeric ligand indicate tetragonal type symmetry about the Cu(II) ions [20]. The spectra obtained are clearly anisotropic and can be the case in which the metal ions are bound directly to the polymeric ligand [21]. The EPR parameters showed that there is an unpaired electron in the dx^2-y^2 orbital. The bonding parameter (α^2Cu), of the Cu(II) complexes, which is a measure of the covalency of the in plane σ-bonding of the ligand group with the coordinating metal ion and was calculated by the expression given by Kivelson and Neimen [22]. The expression is based on the Cu(II)-hyperfine tensor $A_{||}$ as

$$\alpha^2Cu = -(A_{||}/0.036) + (g_{||} - 2.002) + (3/7) (g_{\perp} - 2.002) + 0.04$$

The EPR parameters of 2-20 mol% DVB-crosslinked polyacrylamide-supported glycine- Cu(II) complexes were given in Table 1.

Table 1. EPR Parameters of 2-20 mol% DVB-Crosslinked Polyacrylamide-Supported Glycine-Cu(II) Complexes

DVB (mol%)	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	$\alpha\,^2Cu$
2	2.4725	2.0987	171	51	0.7655
4	0.4912	2.0932	176	54	0.7895
8	2.4343	2.0836	154	44	0.7992
12	2.4436	2.0956	160	47	0.7731
20	2.4816	2.0989	173	48	0.8035

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is the most widely used technique to study the shape, size, morphology, and porosity of polymers [23-26]. The change in the surface morphology of the polymeric ligand with complexation has been investigated using this technique.
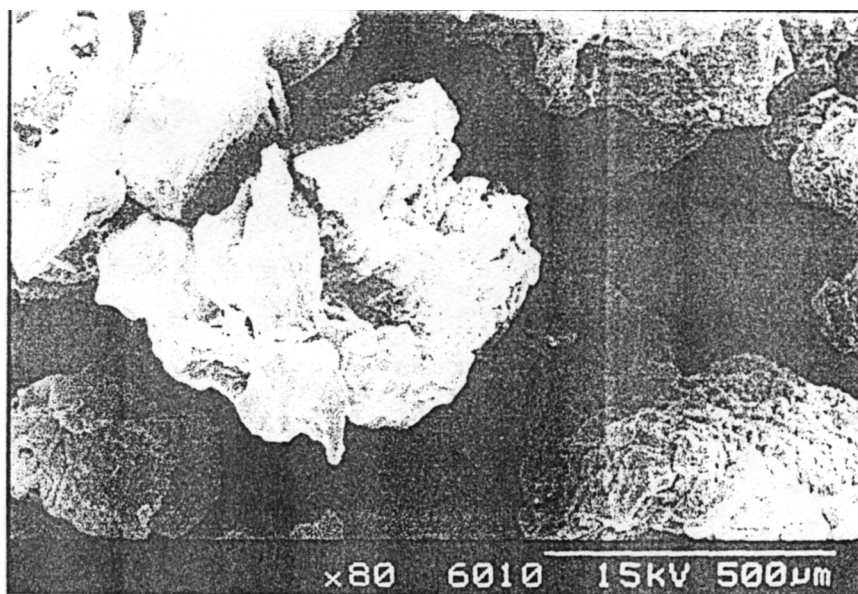
SEM analysis of 4 mol% DVB-crosslinked polyacrylamide-supported glycines and their Cu(II) complexes were used to probe the change in the surface morphological features during complexation. The SEMs of glycine incorporated systems and their Cu(II) complexes are given in Figure 3. The SEMs of uncomplexed resins have smooth surfaces. The voids/channels present in the crosslinked polymer matrix are responsible for the swelling of the polymer and the complexation of the active sites buried with in the three-dimensional crosslinked polymer matrix.

In the Cu(II) complexed resin, the morphology is different from the corresponding uncomplexed resins. In the complexed resin, the voids/channels present in the uncomplexed resin are absent due to the contraction of the voids by the cooperative contribution of the ligands for complexation with Cu(II) ion and surface becomes rough and rigid.

Effect of pH Dependence on Metal Ion Binding

The equilibrium pH of the medium has a significant effect on the specific and selective complexing properties of polymeric ligands and this can be used for the selective separation of metal ions from a mixture of metal ions. The effect of pH dependence on the complexation of various metal ions with the DVB-crosslinked (4 mol%) polyacrylamide-supported glycines is depicted in Figure 4.

The results of the pH studies revealed that at lower pH values, the non-ionic bonding mechanism (e.g. hydrogen bonding) occurs and this lowers the metal ion binding. Since the dissociation of carboxylate group will favour in alkaline pH region, high metal ion binding would take place at higher pH values. Similar

(a)
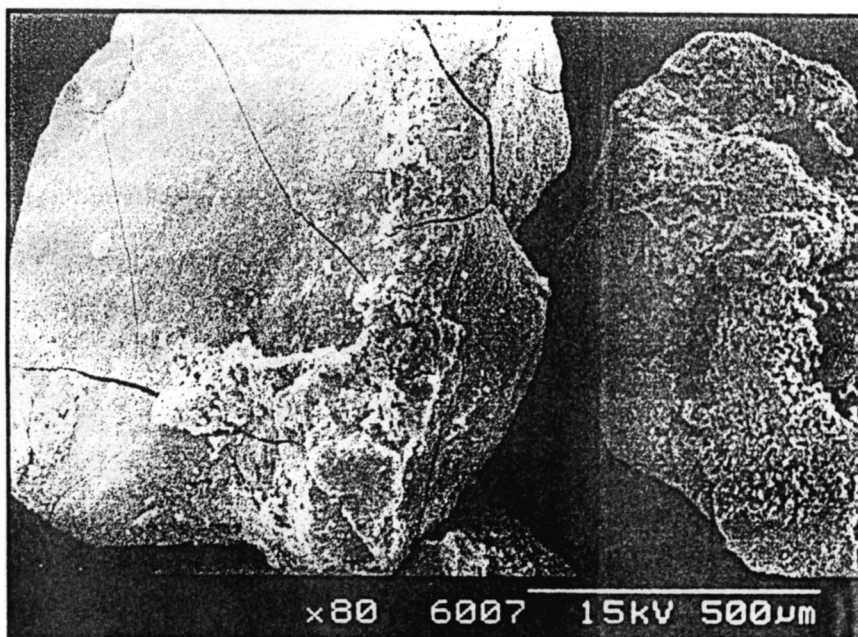
(b)

Figure 3. SEM of (a) 4 mol% DVB-crosslinked polyacrylamide-supported glycine and (b) Cu(II) complex.

Figure 4. pH dependence on the metal ion binding of 4 mol% DVB-crosslinked polyacrylamide-supported glycines.

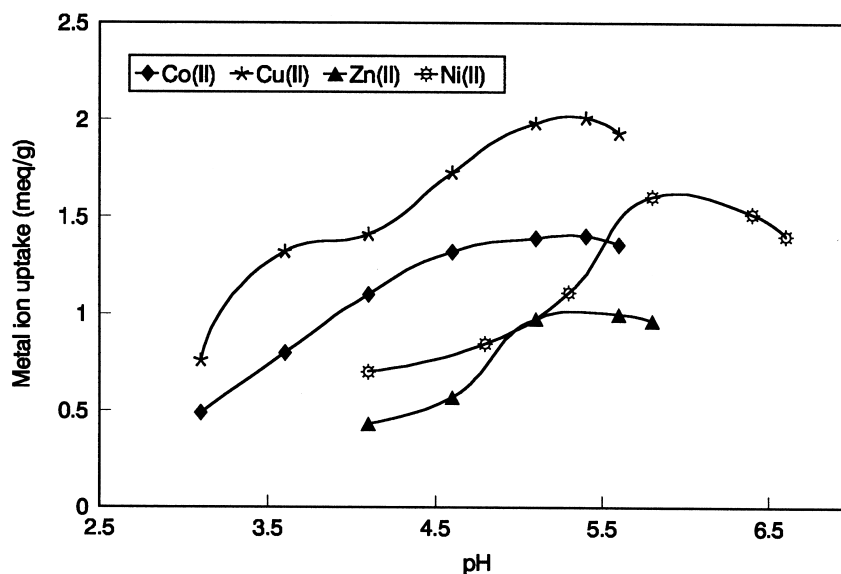observations are reported in the binding of ZrO_2 by polyacrylamide [27]. The results indicate that the optimum pH for different metal ions are: Co (II): 5.4, Cu(II): 5.4, Ni(II): 6.1, and Zn(II):5.6.

Swelling Studies of 2-20 mol% DVB-Crosslinked Polyacrylamides, Polyacrylamide-Supported Glycine, and Cu(II)-Complexes

For a crosslinked polymer, the extent of swelling depends on the solvent-polymer interaction which is determined not only by the nature of the solvent and polymer matrix but also by the active groups introduced into the polymer-matrix. The presence of hydrophobic or hydrophilic crosslinking agents would lead to the formation of crosslinked systems with varying solvation and swelling characteristics.

The swelling characteristics of 2-20 mol% DVB-crosslinked polyacrylamides, crosslinked polymeric ligand and its metal complexes varied with the extent of crosslinking as shown in Figure 5. In the case of hydrophobic DVB-crosslinked systems, the EWC values are very low. As the crosslink density increases the decrease in equilibrium water content (EWC) is very sharp. This considerable decrease in swelling with increasing DVB crosslinking is obvious because DVB imparts more rigidity and hydrophobicity and this increases with increasing concentration of DVB crosslinks in the polymer matrix.

The polyacrylamide-supported glycine ligands showed higher swelling compared to the unfunctionalized polymer due to the increase in the polarity of the
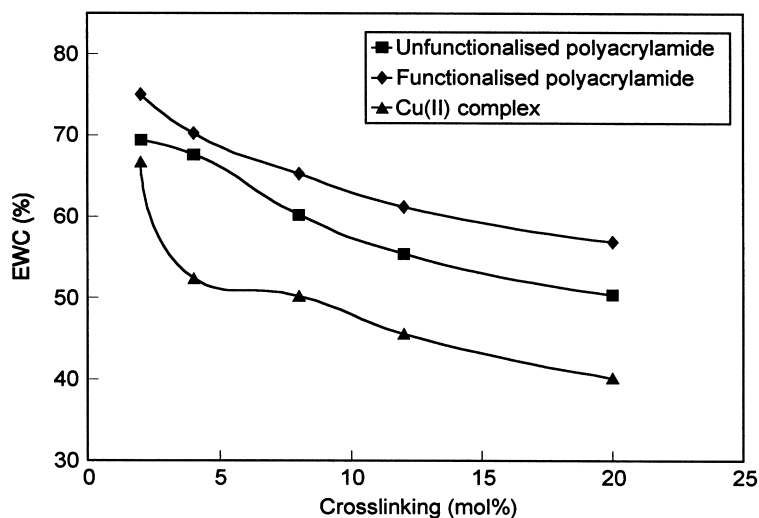
Figure 5. EWCs of 2-20 mol% DVB-crosslinked unfunctionalized and functionalized polyacrylamides, and Cu(II) complexes.

system due to the presence of carboxylate functions. In the metal ion complexed state, the ligand groups are less amenable for binding with water, and hence, the reduction in EWC values is understandable. Moreover, metal ion complexation act as additional crosslinking, leading to strong chain contraction eventually resulting in decreased swelling of the polymer [28].

Metal Ion Rebinding Studies of Metal Ion-Desorbed Systems

In the metal ion complexation of polymer-supported ligands, the polymer chains undergo some sort of rearrangement from their normal position for creating an optimum coordination geometry for metal ion complexation. In the rebinding experimental conditions, if this coordination geometry is not disturbed, the metal ion-desorbed polymers would have certain fixed holes or pockets left by the desorbed metal ions. In order to investigate the specific complexing ability of metal ion-desorbed polyacrylamide-supported glycine ligands, the complexed metal ions were desorbed using 2N H_2SO_4. The neutralized, acid treated polymeric ligands were treated with desorbed metal ions and other metal ions. On metal ion desorption, certain cavities or pockets are developed which is the coordination geometry of the desorbed metal ion. If these *pockets* were not disturbed during the rebinding experimental conditions, they would have an unusual memory for the desorbed metal ion resulting in its specific rebinding as shown in Scheme 3. The accessibility of the undisturbed binding sites around the *pockets* left by the desorbed metal ion depends on the stability of the polymer support. This stability depends on the macromolecular characteristics like nature of the

POLYMERIC LIGAND

POLYMER
METAL COMPLEX

M^{2+}

2N H_2SO_4

M^{2+}

2 N NaOH

POLYMERIC LIGAND

PROTONIZED
POLYMERIC LIGAND
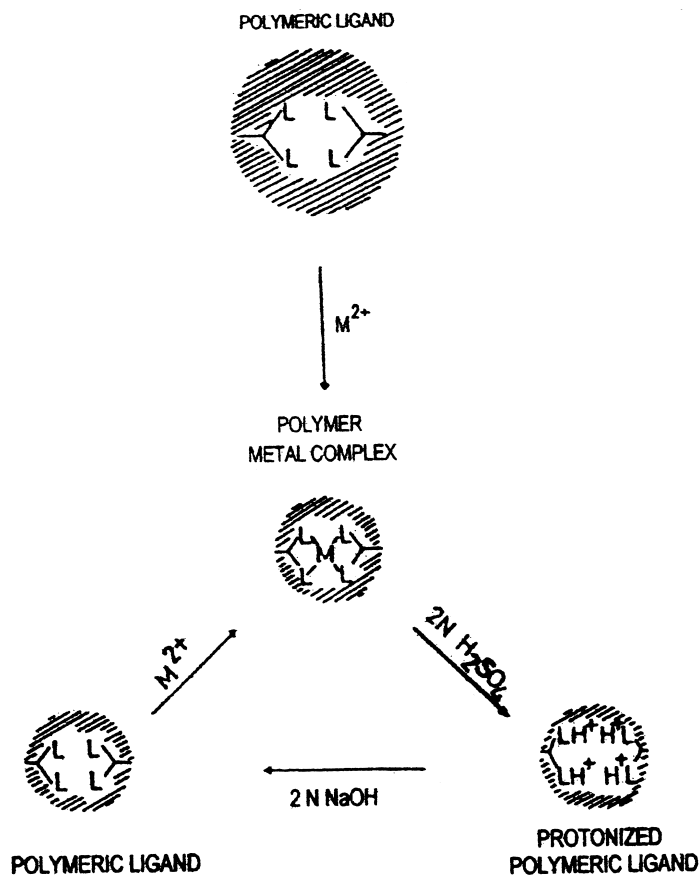
Scheme 3. Specific metal ion rebinding of the metal ion-desorbed systems.

polymer backbone and nature and degree of crosslinking. The polymeric ligands can be brought to the best conformation for the coordination sphere of a metal ion by adjusting the degree of the crosslinking agent [29, 30].

The tendency of this metal ion-desorbed systems to complex with other metal ions is poor compared to their initial complexation. This supports the memory of the metal ion-desorbed systems for the desorbed metal ion, resulting in its specific rebinding. This specificity arises from the difference in the coordination geometries, as well as the difference in size between the desorbed metal ions and other metal ions.

In the DVB-crosslinked polyacrylamide-supported glycines, the metal ion-desorbed resins rebind the desorbed metal ions quantitatively. This specific binding occurred as a result of the rigid and hydrophobic nature of the polymer backbone to keep the cavities of the original metal ion without any deformation. This specific metal ion binding is represented as bold entries in Table 2. The specificity characteristics was found to be increasing with increasing degree of crosslinking

Table 2. Metal Ion Specificity Studies of 2-20 mol% DVB-Crosslinked Polyacrylamide-Supported Glycines

DVB mol%	Desorbed Metal Ion	Metal ion uptake on rebinding* (meq/g)				Original metal ion uptake (meq/g)
		Co(II)	Ni(II)	Cu(II)	Zn(II)	
2	Co(II)	**1.43±0.012** **(98.6%)**	0.98±0.011 (58.6%)	1.52±0.013 (59.8%)	0.59±0.010 (52.6%)	1.45
	Ni(II)	0.76±0.014 (52.4%)	**1.6±0.010** **(95.8%)**	1.49±0.012 (58.6%)	0.64±0.016 (57.2%)	1.67
	Cu(II)	0.85±0.015 (59.2%)	0.91±0.019 (54.4%)	**2.51±0.011** **(98.9%)**	0.58±0.016 (52.2%)	2.54
	Zn(II)	0.76±0.010 (52.5%)	0.84±0.012 (50.2%)	1.50±0.015 (59.0%)	**1.09±0.014** **(97.3%)**	1.12
4	Co(II)	**1.38±0.019** **(99.2%)**	0.81±0.016 (52.6%)	1.19±0.015 (58.3%)	0.48±0.011 (48.5%)	1.39
	Ni(II)	0.84±0.010 (60.4%)	**1.53±0.012** **(98.9%)**	1.14±0.014 (55.8%)	0.57±0.017 (56.4%)	1.54
	Cu(II)	0.77±0.012 (55.4%)	0.81±01.2 (52.5%)	**2.03±0.010** **(99.5%)**	1.04±0.012 (51.6%)	2.04
	Zn(II)	0.71±0.012 (51.0%)	0.65±0.014 (42.2%)	0.92±0.016 (45.1%)	**0.97±01.7** **(98.2%)**	0.99
8	Co(II)	**1.20±0.016** **(99.2%)**	0.75±1.013 (51.3%)	0.98±0.014 (49.4%)	0.43±0.015 (48.7%)	1.21
	Ni(II)	0.60±0.013 (49.5%)	**1.45±0.014** **(99.3%)**	0.99±0.018 (50.0%)	0.44±0.019 (49.7%)	1.46
	Cu(II)	0.59±0.019 (48.7%)	0.69±0.014 (47.0%)	**1.96±0.016** **(99.4%)**	0.42±0.015 (46.9%)	1.98
	Zn(II)	0.57±0.015 (47.1%)	0.71±0.012 (48.6%)	0.98±0.013 (49.9%)	**0.88±0.012** **(98.9%)**	0.89
12	Co(II)	**1.14±0.013** **(99.5%)**	0.66±0.013 (48.8%)	0.88 ±0.015 (48.3%)	0.35±10.13 (47.6%)	1.15
	Ni(II)	0.56±0.012 (48.6%)	**1.34±0.014** **(99.3%)**	0.87±0.013 (47.8%)	0.34±0.016 (46.2%)	1.35
	Cu(II)	0.54±0.013 (46.9%)	0.57±0.014 (42.2%)	**1.81±0.016** **(99.5%)**	0.32±0.014 (43.2%)	1.82
	Zn(II)	0.52±0.014 (45.2%)	0.58±0.013 (42.9%)	0.81±0.017 (44.5%)	**0.74±0.012** **(99.1%)**	0.75
20	Co(II)	**1.01±0.013** **(99.6%)**	0.58±0.014 (46.7%)	0.77±0.015 (49.7%)	0.27± 0.012 (42.1%)	1.02
	Ni(II)	0.42±0.012 (41.1%)	**1.23±0.018** **(99.5%)**	0.73±0.019 (42.4%)	0.26±0.015 (41.2%)	1.24
20	Cu(II)	0.48±0.013 (47.0%)	0.52±0.016 (41.9%)	**1.716±0.015** **(99.8%)**	0.26±0.018 (40.6%)	1.72
	Zn(II)	0.46±0.014 (45.6%)	0.57±0.013 (46.1%)	0.76±0.015 (45.9%)	**0.63±0.012** **(99.2%)**	0.64

[a]Average of three experiments; values in parenthesis show the percentage of metal intake.

from 2-20 mol%. The 2 mol% systems had the lower rebinding capacity than the higher crosslinked systems. For a crosslinked polymer, the mechanical stability increases with increasing degree of crosslinking. This reduces the extent of deformation of the developed *cavities* during the metal ion desorption experimental conditions. Thus, the possibility of maintaining the stable geometry for the desorbed metal ion with increasing rigidity of the polymer support. These newly developed resins have more enhanced specificity characteristics than our previously reported N,N'-methylene-bis-acrylamide-crosslinked systems. This is due to more stability of the rigid DVB-crosslinked system than the semi-rigid and flexible NNMBA-crosslinked system.

pH Dependence on Metal Ion Rebinding

In order to investigate the pH dependence on metal ion rebinding, the complexation of 4 mol% DVB-crosslinked polyacrylamide-supported glycine metal ion-desorbed systems were carried out at different pH values and found that pH has no significant effect on metal ion rebinding. This points to the fact that the specific metal ion rebinding is solely determined by the memory of the fixed geometry kept in the three-dimensional polymer matrix. However, in the case of rebinding of Co(II) ions using Co(II)-desorbed resins, no considerable difference was noted from the original binding. This suggests that the pH has no significant effect on Co(II) ion rebinding (Figure 6). The same was observed in the case of Cu(II) ion rebinding of the Cu(II) ion-desorbed resins.
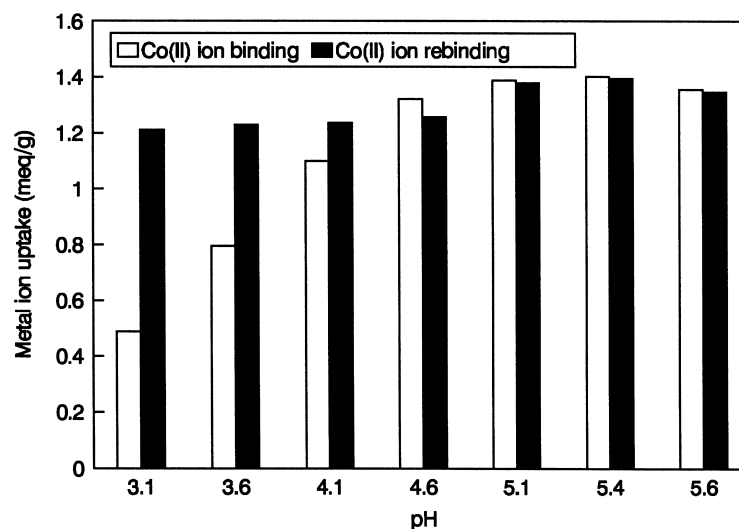

Figure 6.   pH dependence on the Co(II) rebinding of 4 mol% DVB-crosslinked polyacrylamide-supported glycine.

Time-Course and Kinetics of Metal Ion Binding and Rebinding

Time-Course of Metal Ion Binding and Rebinding

The macromolecular characteristics like the nature of the polymer backbone and the degree of the crosslinking significantly affects the kinetics of metal ion complexation. In order to follow the time-course and kinetic parameters of Cu(II) ion binding and rebinding by 2-20 mol% DVB-crosslinked polyacrylamides, polymers with 200-400 mesh size were selected. Definite amounts, of the insoluble ligands were equilibrated with Cu(II) salt solution (0.05 N) in a thermostatically controlled system and the amounts of Cu(II) ion bound was followed at regular intervals of time. Figure 7 shows the time-course of Cu(II) ion binding by 4 mol% DVB-crosslinked polyacrylamide-supported glycines. In order to evaluate the efficiency of the polymeric ligand for the selective and fast rebinding of metal ions, metal ion binding and rebinding experiments were carried out for the Cu(II) complexation of 4 mol% DVB-crosslinked polyacrylamide-supported glycines. The time required for the original copper ion complexation for DVB was 2.5 hours. For rebinding, it requires only 1 hour with a $t_{1/2}$ of 0.5 hours. This indicates the development of a favorable stable geometry for the metal ion-desorbed polymer resulting in its fast rebinding.

Kinetics of Metal Ion Binding and Rebinding

The kinetics of Cu(II) ion binding by the 2-20 mol% DVB-crosslinked systems were followed by equilibrating the polymeric ligands with Cu(II) salt solu-
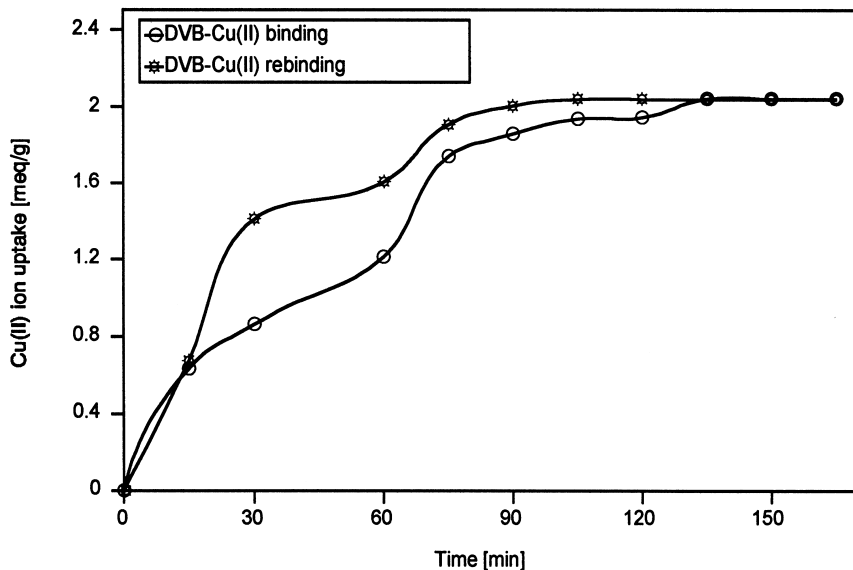

Figure 7. Time-course of Cu(II) ion binding and rebinding of 4 mol% DVB-crosslinked polyacrylamide-supported glycines.

Table 3. Kinetic Parameters of Cu(II) Ion Binding of 2-20 mol% DVB-Crosslinked System

Crosslinking (mol%)	ΔE (kJ/mol)	ΔS (J)	A (s^{-1})
2	20.56	−279.87	1.53×10^{-2}
4	41.69	−202.40	1.51×10^{-2}
8	43.70	−282.33	1.40×10^{-2}
12	44.96	−281.36	1.26×10^{-2}
20	52.16	−282.88	1.13×10^{-2}

tions at 304 and 313 K for varying time intervals. The kinetic parameters were calculated using the Arrhenius equation and are given in Table 3.

The results showed that the activation energy required for complexation increases as the degree of crosslinking increases from 2 to 20 mol%. With an increasing degree of crosslinking, the availability of the ligand groups for complexation was found to be less. Moreover, the penetration of the metal ions into polymer matrix becomes less or hindered due to the increased rigidity of crosslinking, requiring a longer reaction time and higher activation energy.

For the Cu (II) ion rebinding of 4 mol% DVB-crosslinked metal ion-desorbed system, the activation energy required for the DVB-crosslinked polyacrylamide system is much less (Figure 8). This also points to a more favorable and stable geometry kept in the rigid DVB-crosslinked system. The higher activation energy required for the initial complexation is for the adjustment of the macro-
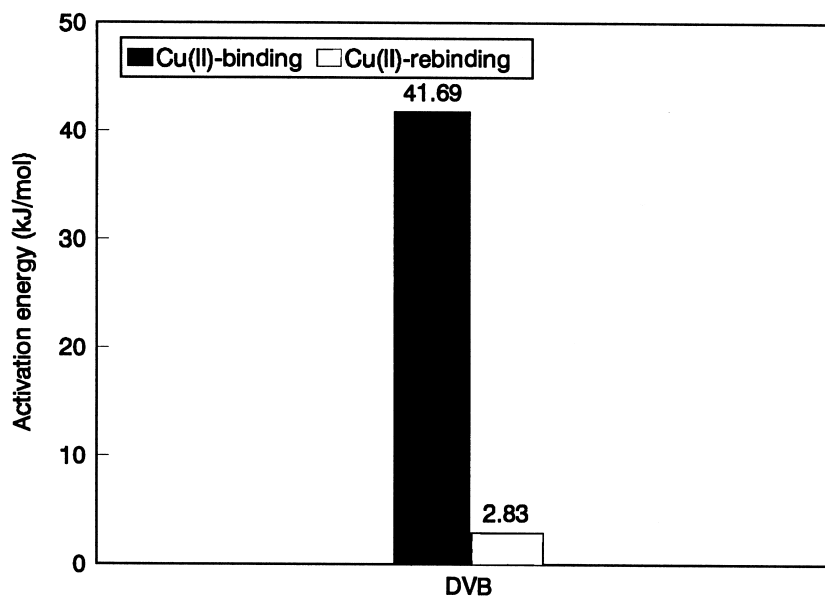
Figure 8. Activation energy for Cu(II) ion binding and rebinding.

molecular chains from their normal position for creating the required geometry for the complexed metal ions. Generally, the polymeric ligands undergo rearrangment for metal ion binding and if these coordination geometries were not disturbed during the rebinding process it would result in fast rebinding. Thus, a very low activation energy is only required for metal ion rebinding.

Metal Ion Selectivity Studies of Polyacrylamide-Supported Glycines and Their Metal Ion-Desorbed Systems

In order to investigate the selectivity characteristics of 2-20 mol% metal ion-desorbed DVB-crosslinked polyacrylamide-supported sodium salt of glycines, competitive rebinding experiments were carried out with pairs of metal ions at its natural pH. The metal ion-desorbed systems showed a higher selectivity towards the desorbed metal ion from a mixture of metal ions. The size of the metal ion, and the difference in the coordination geometry of the various polymer-metal complexes are decisive in dictating this selectivity. Under the conditions of selectivity studies, when the polymeric ligand is subjected to vigorous stirring, metal ion binding without any selectivity was observed. This is due to the disruption of the orientation of coordination geometry of the desorbed metal ions sculpt in the solid polymer matrix.
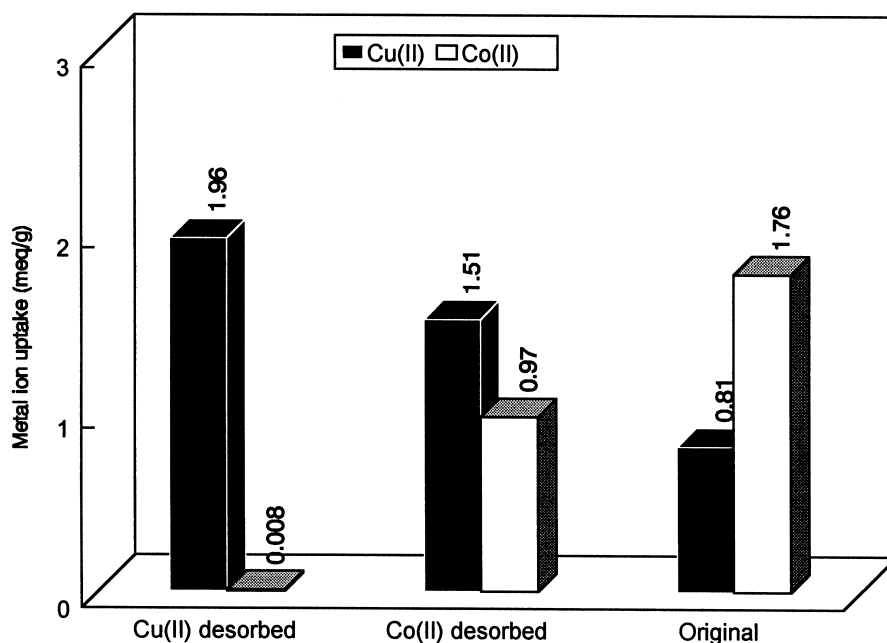

Figure 9. Selective Cu(II) ion rebinding of 4 mol% DVB-crosslinked polyacrylamide-supported glycines.

The selectivity studies of the Co(II), Ni(II) and Cu(II)-desorbed DVB-crosslinked polyacrylamides were carried out with Co(II)-Cu(II); Cu(II)-Ni(II); Cu(II)-Co(II) pairs of metal ions. The results are summarized in Table 4. In all these cases, the metal ion-desorbed resins showed a higher selectivity for its desorbed metal ions. This selectivity is higher for the Cu(II) or Co(II)-desorbed systems for a Cu(II)-Co(II) mixture than the Ni(II)-desorbed system for a Cu(II)-Ni(II) mixture. This is because of the size difference between the two metal ions as well as the difference in geometry between the two complexes. The results of the selective rebinding of Cu(II) ions by the 4 mol% crosslinked system is given in

Table 4. Summary of Selectivity Studies of 2-20 mol% DVB-Crosslinked Polyacrylamide-Supported Glycine (Original and Metal Ion-Desorbed Systems)

DVB (mol%)	Desorbed metal ion	Rebinding pair of metal ions	Metal ion complexation of desorbed system from the mixture[a]	Original complexation (meq/g)
2	Co(II)	Co(II)+Cu(II)	Co(II)=0.92, Cu(II)=0.64	1.45
	Ni(II)	Cu(II)+Ni(II)	Cu(II)=1.24, Ni(II)=0.76	1.67
	Cu(II)	Cu(II)+Co(II)	Co(II)=0.01 Cu(II)=2.24	2.54
	Cu(II)	Cu(II)+Ni(II)	Cu(II)=1.96, Ni(II)=0.56	2.54
Original polymer	Nil	Cu(II)+Co(II)	Co(II)=0.56, Cu(II)=1.07	—
	Nil	Cu(II)+Ni(II)	Cu(II)=1.56, Ni(II)=0.44	—
4	Co(II)	Co(II)+Cu(II)	Co(II)=0.97, Cu(II)=1.51	1.39
	Ni(II)	Cu(II)+Ni(II)	Cu(II)=1.19, Ni(II)=0.90	1.54
	Cu(II)	Cu(II)+Co(II)	Co(II)=0.008,Cu(II)=1.96	2.04
	Cu(II)	Cu(II)+Ni(II)	Cu(II)=1.06, Ni(II)=0.92	2.04
Original polymer	Nil	Cu(II)+Co(II)	Co(II)=0.81, Cu(II)=1.76	—
	Nil	Cu(II)+Ni(II)	Cu(II)=1.37, Ni(II)=1.30	—
8	Co(II)	Co(II)+Cu(II)	Co(II)=0.99, Cu(II)=0.56	1.21
	Ni(II)	Cu(II)+Ni(II)	Cu(II)=1.02, Ni(II)=0.89	1.46
	Cu(II)	Cu(II)+Co(II)	Co(II)=0.007,Cu(II)=1.87	1.98
	Cu(II)	Cu(II)+Ni(II)	Cu(II)=1.27, Ni(II)=0.74	1.98
Original polymer	Nil	Cu(II)+Co(II)	Co(II)=1.56, Cu(II)=0.64	—
	Nil	Cu(II)+Ni(II)	Cu(II)=1.61, Ni(II)=0.46	—
12	Co(II)	Co(II)+Cu(II)	Co(II)=1.01, Cu(II)=0.67	1.15
	Ni(II)	Cu(II)+Ni(II)	Cu(II)=0.97, Ni(II)=0.76	1.35
	Cu(II)	Cu(II)+Co(II)	Co(II)=0.003,Cu(II)=1.79	1.82
	Cu(II)	Cu(II)+Ni(II)	Cu(II)=0.97, Ni(II)=0.67	1.82
Original polymer	Nil	Cu(II)+Co(II)	Co(II)=0.67, Cu(II)=1.56	—
	Nil	Cu(II)+Ni(II)	Cu(II)=1.67, Ni(II)=0.82	—
20	Co(II)	Co(II)+Cu(II)	Co(II)=0.87, Cu(II)=0.72	1.02
	Ni(II)	Cu(II)+Ni(II)	Cu(II)=0.72, Ni(II)=0.62	1.24
	Cu(II)	Cu(II)+Co(II)	Co(II)=0.002, Cu(II)=1.67	1.72
	Cu(II)	Cu(II)+Ni(II)	Cu(II)=0.82, Ni(II)=0.74	1.72
Original polymer	Nil	Cu(II)+Co(II)	Co(II)=0.57, Cu(II)=1.02	—
	Nil	Cu(II)+Ni(II)	Cu(II)=1.26, Ni(II)=0.72	—

[a]Average of three experiments.

Figure 9. The selectivity characteristics was found to be increasing with increasing degree of crosslinking. An increasing degree of the crosslinking, the geometry of the binding site for favorable complexation becomes more stable, and this is even higher in the rigid DVB-crosslinked system. Thus, the specific complexation behavior of the Cu(II)-ion desorbed polyacrylamide-supported system can be exploited for the selective concentration of the desorbed Cu(II) ions from a mixture of Cu(II) and Co(II) ions. By the suitable selection of the crosslinking agents and by controlling the degree of crosslinking it is possible to design metal ion specific polymers

CONCLUSION

The present study helps to design a better and efficient metal ion selective polymeric system which effectively rebind the desorbed metal ion from a mixture of metal ions. The nature and degree of the crosslinking agent solely controlled the metal ion complexation and rebinding. The observed trend in complexation was: Cu(II) > Ni(II)> Co(II)> Zn(II) and the metal ion complexation is less as the degree of DVB-crosslinking increases from 2-20 mol%. The metal ion uptake decreases in the acidic pH, shows a maximum and again decreases. The pH has no significant effect on metal ion rebinding. The kinetic parameters are in agreement with first order reaction kinetics. The time required for metal ion rebinding is much less than that required for its first metal ion binding. The activation energy required for metal ion rebinding is also much less than that required for binding. The metal ion specificity and selectivity studies clearly verified the memory effect of the metal ion-desorbed polymer. The metal ion-desorbed resins showed enhanced specificity for the desorbed metal ions. On the other hand, no specificity was observed for the binding of other metal ions. The Cu(II) ion-desorbed system selectively binds Cu(II) ions from a mixture of Cu(II) and Co(II) ions. In the case of the Cu(II) and Ni(II) system, even though a slight selectivity for the desorbed Cu(II) was observed, a complete separation was not achieved.

ACKNOWLEDGMENT

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